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The Effect of Temperature on the Rate of Dissolution of Gold in Cyanide Solutions which have a Constant Oxygen Content.

Robert Currie

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A Thesis

Submitted to the Department of Metallurgy

in Partial Fulfillment of the

Requirements for the Degree of

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MONTANA SCHOOL OF MINES

BUTTE, MONTANA

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CONTENTS

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Introduction

Since the development of cyanidation into a highly efficient process for treating gold ores, many papers have been written on its various aspects. Although, there has been much work done on it, the chemistry of the reaction is not yet completely understood. One of the more interesting phases of the problem is the effect of temperature and oxygen concentration on the rate of dissolution of a soluble metal. It has been shown that an increase of temperature, and also an increase of oxygen concentration will materially increase the rate of dissolution. However, an increase in temperature will decrease the amount of oxygen which a given amount of solution will dissolve, so to understand clearly what happens, two problems present themselves. These are: (1) the effect of an increase in oxygen concentration at constant temperature and (2) the effect of an increase in temperature at constant oxygen concentration. The former problem has been solved--the latter comprises this thesis.[1]

History

The first cyanide compound, prussion blue, was discovered in Germany in 1704, by a dye chemist. About one hundred years later it was discovered that a dilute cyanide solution would dissolve metallic gold. This fact was regarded with no especial interest until in 1867,[2] a patent was taken out for a process whereby a method for treatment of auriferous and argentiferous ores was expounded. Due to this interesting and valuable application a new impetus was given to men of science to further investigate the cyanide reaction. And in the years after 1867, many experiments were performed and reported. Due to his interest in the subject and probably helped by preceding investigators, John Stewart MacArthur[3] in 1891 developed the first commercially practical process for cyaniding gold ores. Of course, much research was necessary to perfect the process, and many problems not only practical but of an academic interest were investigated.

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1) J.A. Cook: "A Study of the Effect of Oxygen on the Rate of Dissolution of Gold in Cyanide Solutions" Bachelor's thesis, 1936

2) Julian and Smart: "Cyaniding Gold and Silver Ores" (1)

3) Transactions A.I.M.E., 64,840.

Theory

Cyanide is a compound of the cyanogen radical CN with usually a metallic substance, as potassium (K), forming potassium cyanide (KCN). The radical CN is cyanogen, and it reacts chemically as though it were one single element. It is a most active radical, especially in combining with metals, with which it forms several hundred compounds. Here we are not concerned with this ability. It is only of importance that a dilute solution of potassium cyanide with gold forms a double cyanide of potassium and gold which is soluble.

However, potassium cyanide alone will not dissolve gold. Oxygen and water are also necessary.[1) This is best shown by the following reactions:

(1) $4Au = 4Au^{+} + 4e$

(2) $O_2 + 2H_2O + 4e = 4OH^{-}$

(3) $8KCN = 8K^{+} + 8CN^{-}$

(4) $4Au^{+} + 8CN = 4Au(CN)_2^{-}$

Adding and simplifying the above equations we obtain

$$4Au + 8KCN + O_2 + 2H_2O = 4KAu(CN)_2 + 4KOH$$

This combined reaction is known as Elsner's Equation, and although others have been suggested, it is the one which is generally accepted. From the equation

1) Christy: Transactions A.I.M.E. (1896), 26, 735.

it is seen that oxygen is necessary to dissolve gold.

The solubility of a metal is dependent largely on the amount of ionization of the salt, and on the velocity of the ions. As ionization does not increase, but the solubility of the metal does increase, increased velocity of the ions must transpire with increasing temperatures.[1)]

Method

Experiments have shown that pure gold dissolves most rapidly in a solution of 0.25 per cent KCN,[2)] and also that at concentrations of cyanide less than two per cent the solubility of oxygen in the solution is not affected.[3)]

The shape of the metal to be used in an experiment such as this, has an important bearing on the rate of dissolution. To do reliable work the particles of gold to be tested must be as nearly identical as possible. The area exposed to the solvent action of the cyanide must be constant, and it follows that the shape of particles which would allow the area exposed to remain constant is a thin disk. It is

1) Amer. Chem. Jour., Vol.26, No.5, Nov. 1901.

2) Jour. Chem. Soc., Vols.67,68. pp. 199-212.

3) Barsky, Swainson, and Hedley, Trans. A.I.M.E. (1934) 212

evident that, under the same solvent conditions, the quantity dissolved would be in direct proportion to the time. To further emphasize this point it can be shown that while a thin gold disk would lose weight in a cyanide solution at a definite rate, gold particles in a spherical shape would, assuming again uniform solvent conditions, lose weight in a changing rate.[1)] In each equal interval of time a spherical shell of equal thickness would be dissolved, but each successive shell would be of smaller diameter, and would contain a smaller amount of gold. Figure 1 page 6, shows the rates of dissolution of gold when in the shape of thin disks and in the shape of spheres.

Gold disks were made in the following manner. The gold was carefully rolled out in a thin sheet of uniform thickness and disks were punched from the sheet. These were then heated to a red heat so that any irregularities in the surface from the cutting were rounded. Then they were weighed and those that showed too much irregularity in weight were not used.

The solutions used were made by mixing oxygen

1) Julian and Smart, Cyaniding Gold and Silver Ores,92

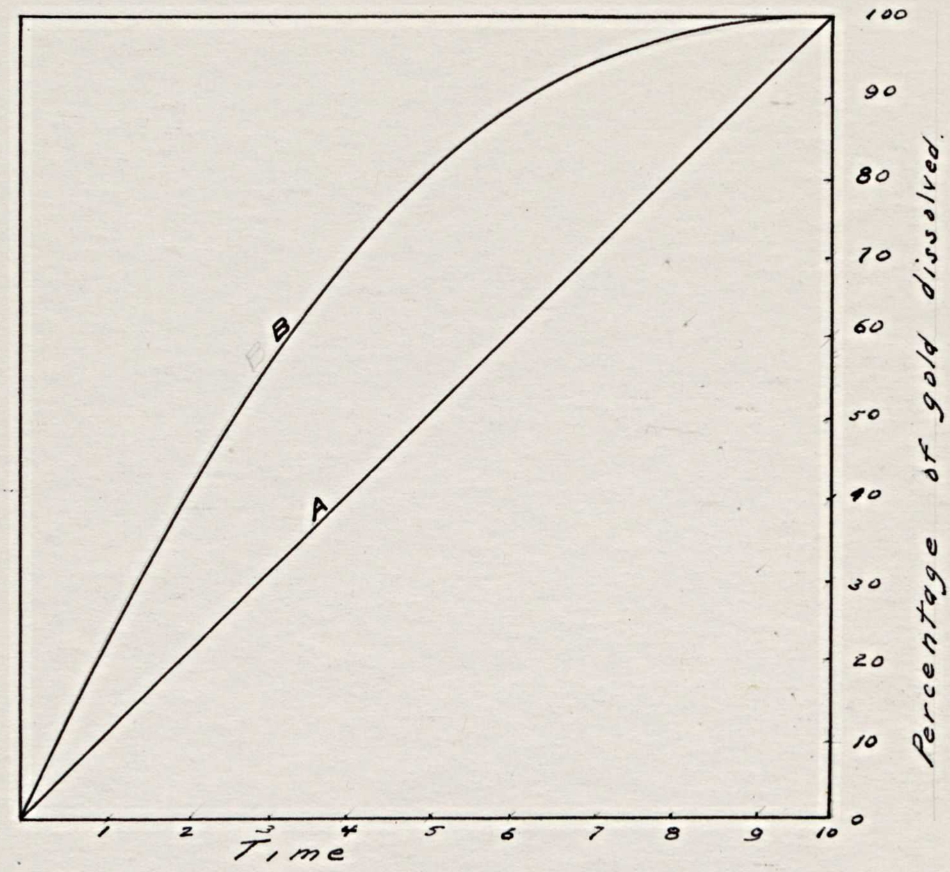

Figure 1. - Curve A shows the rate of dissolution of thin gold plates where the surface exposed to the solution is practically constant. Curve B shows the rate of dissolution where the gold is in the form of spheres.

free water and oxygen saturated water. Oxygen free water was prepared by boiling distilled water in a train of liter flasks for an hour. They were then placed under an atmosphere of natural gas. The flasks in the train were connected with two-hole rubber stoppers and glass tubing. At each end of the train a pinchcock was attached. The flasks were filled with water, placed on the hot plate, and allowed to boil for an hour, with one pinchcock closed. The steam from the flask at the pinchcock was passed from the flask through a glass tube to the bottom of the following one, from there it bubbled through the water of the second flask and was forced in a like manner through all the following flasks. After the water had been boiled for an hour, the exhaust pinchcock was closed, and the train was removed from the hot plate and connected to a gas jet. As the water cooled, the steam condensed and the vacuum thus formed drew the water from each preceding flask opposite in direction to that in which the steam was evolved. The end flask was then half filled with water and half with gas, the other flasks being completely filled with oxygen free water. When the water had cooled to room temperature, it was ready for use; the pressure of the gas from the main would force the water out when both pinchcocks were opened.

Oxygen saturated water is that water which at the prevailing atmospheric pressure, and at room temperature is completely saturated with air. If the atmosphere above the water were pure oxygen there would be much more oxygen dissolved, for according to Dalton's law[1] the amount of each gas dissolved from a mixture of gases depends on the partial pressure of that gas. To prepare the water air was bubbled through the two liter flask which was three quarters full. The air was bubbled through the water for an hour, and then it was allowed to stand for an hour. The solubility of oxygen in water was obtained from the tables of the Handbook of Chemistry and Physics. At 20 degrees centigrade and 760 millimeters pressure it was found that saturated water under an atmosphere of pure oxygen contained 43.39 milligrams per liter. The barometric pressure at the time of the experiment was 618 mm. of mercury and the vapor pressure of water was 17.36 mm.

To find the amount of oxygen dissolved from air

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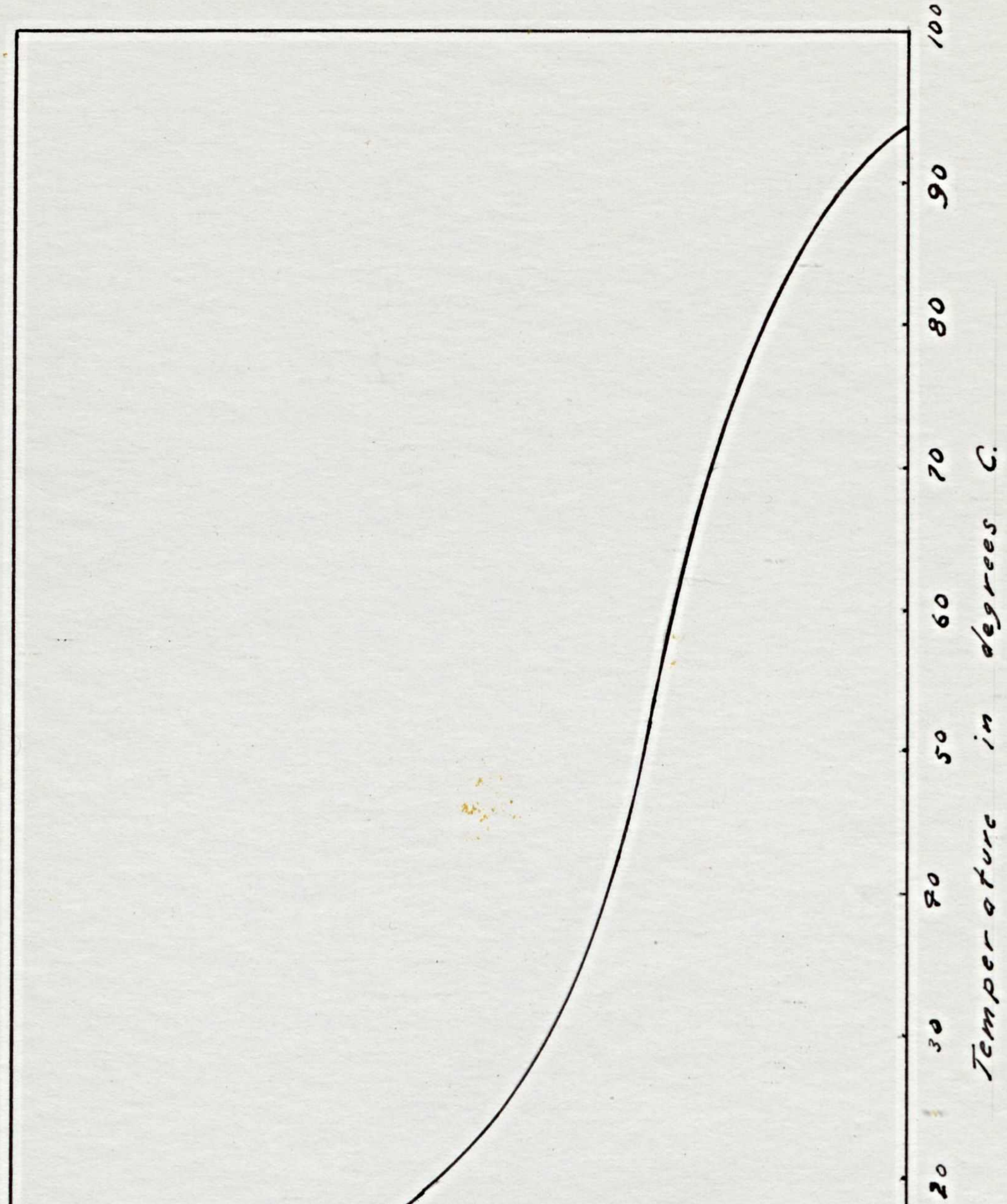
1) Getman and Daniels, Outlines of Theoretical Chemistry, 142.

the following calculation is made:

$$0.209 \times \frac{(618 - 17.36)}{(760 - 17.36)} \times 43.39 = 7.335 \text{ mg. per liter}$$

To determine a suitable range of temperature variation it was necessary to consult a chart showing the solubility of oxygen in water from air at the elevation of Butte at different temperatures. This chart is shown on page 10, figure 2. If a concentration of 3 mg. of oxygen per liter is desired, it is seen from the chart that temperatures exceeding 72 degrees centigrade should be avoided because at higher temperatures than that part of the oxygen will be thrown out of solution and will escape. It was decided to use 3 mg. of oxygen per liter of solution for the investigation. It is a simple calculation to find the amounts of each water needed to have the required oxygen concentration.

Flasks of 500 cc. capacity were used for the agitations. It was decided to stir the solution with motor driven steel rods. Figure 3, page 11, shows a cross section of the bottle used. A layer of a refined mineral oil two centimeters thick was placed on the solution under the cork to insure against additional oxygen being dissolved. The



Oxygen Saturation Curve

Fig. No. 2

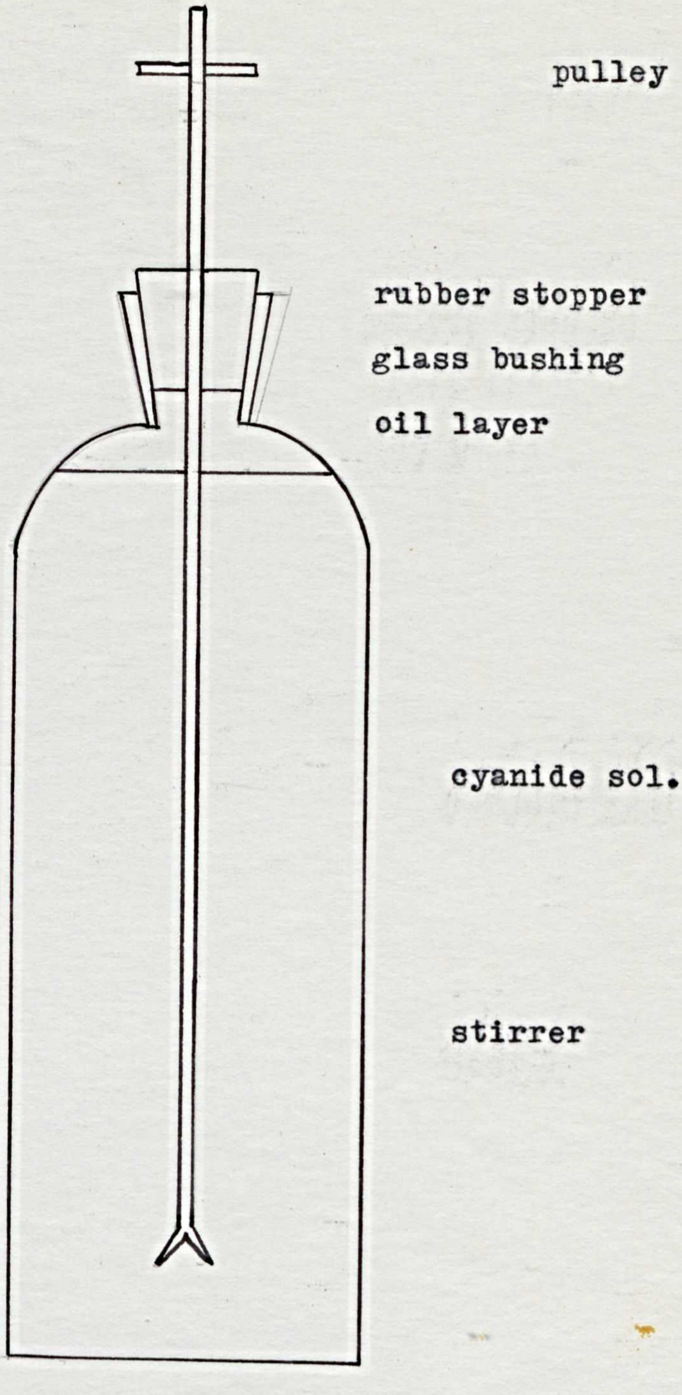


Figure 3. Cross section of the 500 cc. bottle used for the twenty-four hour agitations.

solutions were agitated for twenty-four hours. The bottles were placed in a water bath whose temperature could be kept constant within plus or minus one degree centigrade. After the agitation the gold disks were weighed, and the loss in weight was checked by assaying the solution. Several of the solutions were analyzed for oxygen to see if additional amounts of the gas had been dissolved. The method used was Hamilton's[1] modification of White's procedure and showed no appreciable change in the oxygen content of the solutions after the agitation period. The gold disks had an average weight of 40 mg.

The results of this series of agitations at an oxygen concentration of 3 mg. per liter is shown in Table I.

Table I

Amount of Gold Dissolved in Twenty-four Hours

Temperature	Wt. of Au Dissolved
20 degrees C	0.80 mg.
25 "	0.86 "
30 "	0.90 "
32 "	0.92 "
42 "	0.96 "
48 "	1.11 "

1) E. and M. J., 110, 116.

Table I (cont'd)

Temperature	Wt. of Au Dissolved
55 degrees C.	1.14 mg.
70 "	1.26 "

The above points are plotted on Figure 4, page 14.

A second test was performed in which the gold was weighed during the agitation. An 800cc. bottle with a three hole rubber stopper was used. A thermometer was placed in one of the holes; in one of the others was a steel stirring rod, and in the other was a glass thread from which the gold was suspended. The gold was rolled into a large thin disk weighing 1.5 grams, and this disk was curved into a cylindrical shape. The bottle was placed in the bath, and directly above it was placed a gold balance to which was attached the glass thread from which the gold was suspended. The temperature was varied by means of the thermostat and agitations at each temperature were carried on for fifteen minute periods. The amount of time was quite important in this experiment, so in order not to make mistakes a stop watch was used. It was found that at room temperature the apparatus was not accurate because of the viscous resistance offered to the glass thread which lessened

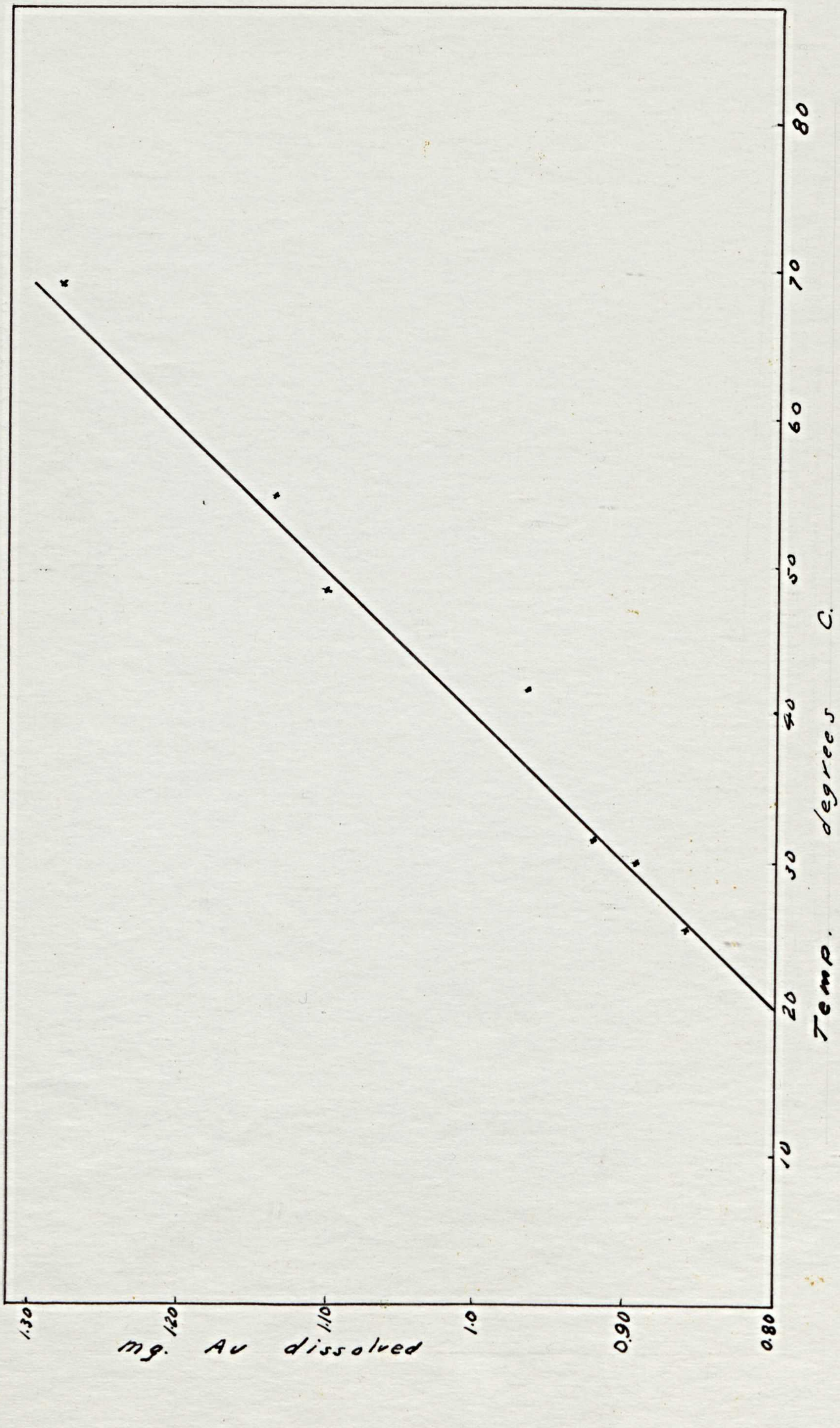


Fig. 4 Amount of Au dissolved in 24 hours.

the sensitivity of the balance. However, at higher temperatures the oil was less viscous and better results were obtained. These are shown in Table II.

Table II.

Amount of Gold Dissolved in Fifteen Minutes.

Temperature	Wt. Au Dissolved
42 degrees C.	0.32 mg.
48 degrees C.	0.58 mg.
53 "	0.68 "
58 "	0.94 "
65 "	1.24 "

These results are shown on Figure 5, page 16.

In both of these tests solutions having a concentration of 0.25% KCN were used.

Conclusions

It is an almost elementary fact that an increased temperature will increase the rate of dissolution of metallic gold in a dilute solution of cyanide. However, no attempt has been made to determine the rate of increase of dissolution controlling the variables of oxygen concentration and temperature simultaneously. The results here show that the rate of solution of the gold varies directly as the temperature.

In mill practice a greater amount of gold will

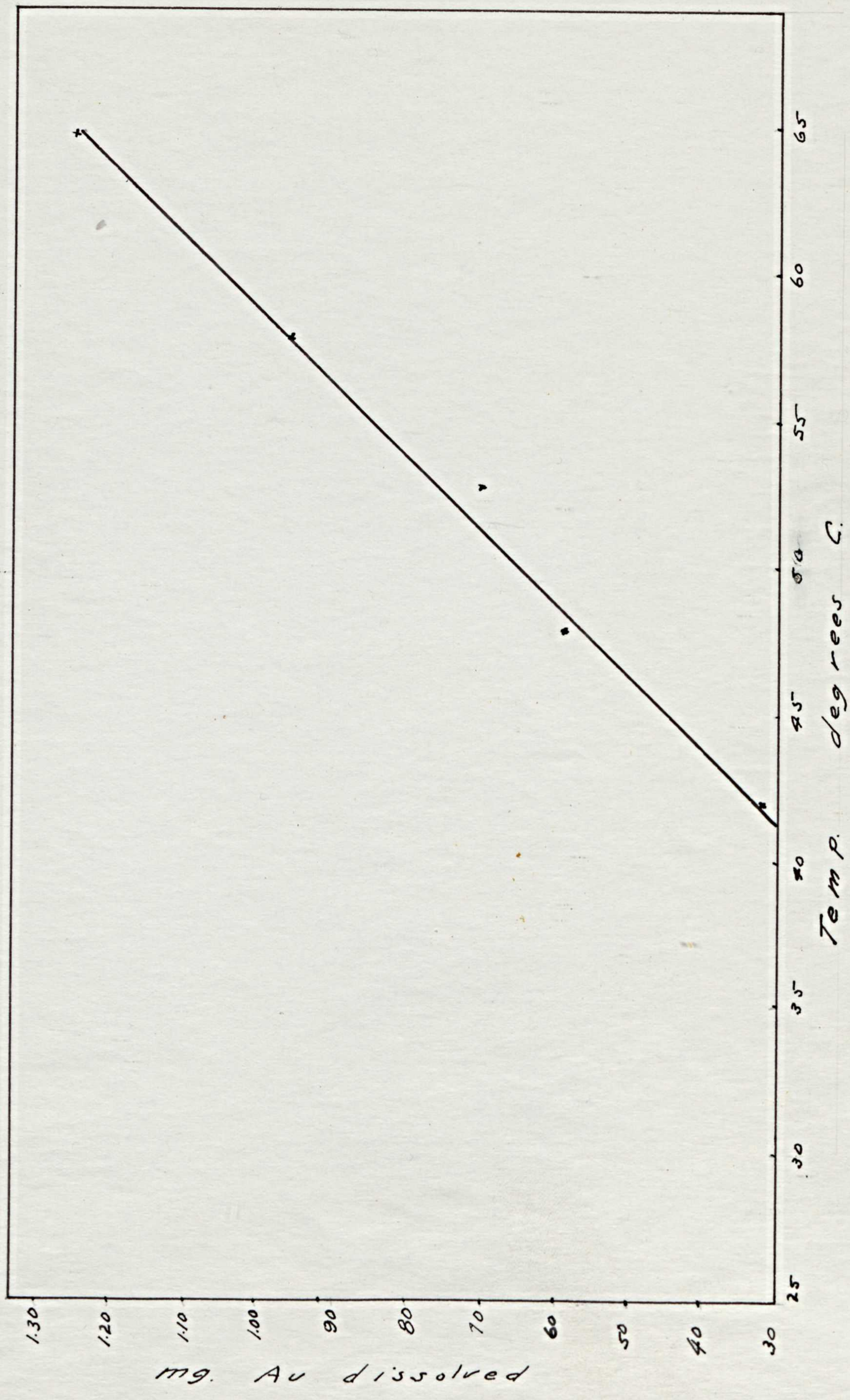


Fig. 5 Amount of Au dissolved in 15 minutes

dissolve in a given time at an increased temperature even though less oxygen would be present in the solution. However, it would not be an economically sound practice to do so, a better way to obtain optimum extraction would be to increase the time of agitation.

Acknowledgment

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